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(An)elastic softening from static grain boundaries and possible effects on seismic wave propagation

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Abstract It is argued that low-frequency wave propagation shows, in most cases, very little dependence on the atomistic properties of grain boundaries if the thickness of the grain boundary is atomistically thin while the grain size is in the mm region. Large effects do exist for specific textures (e.g. the brick wall texture). The essential ingredient for the assessment of an-elastic and non-linear elastic features of seismic wave propagation does not primarily depend on the structural properties of immobile, dry grain boundaries but on the way the grain boundary properties can be related to those of macroscopic mineral assemblies. Specific results for coated sphere textures are derived using Hashin-Shtrikman theory. An-elastic seismic features are more likely to be related to the mobility of boundaries and dislocations which can be attached to the grain boundaries, or bulk-related defect structures, rather than the intrinsic materials properties of the grain boundaries.

Keywords Elasticity · Interfaces · Effective medium theories

Introduction

It is often hoped that the understanding of elastic, an-elastic and visco-elastic behaviour of mineral assemblies helps the geophysical analysis of seismological observations. While elastic behaviour of single crystals (including the highly non-linear behaviour in ferroelastic minerals) is fairly well understood, one struggles with the prediction of the elastic response of mineral assemblies based on appropriate effective medium theories. In addition one is concerned with the condition that the stress fields associated with seismic waves are very small, their frequency is very low and, thus, their wavelength is much longer than any of the structural features discussed in this paper (Jackson and Paterson 1987). This means that we can approximate the dynamics of the wave propagation as quasi-static, i.e. we may ignore features of the wave propagation such as Raleigh scattering. Large-scale topological changes of interfaces between mineral grains can also be excluded on grounds of the low energy input of the seismic wave. The question then arises: does the atomistic structure of the grain boundary or its assembly in a structured medium determine the elastic response of the medium? (Romanowicz and Durek 2000; Andrews et al. 2006). In this paper it is argued that static dry grain boundaries are almost irrelevant unless they form themselves a significant part of the volume of the medium or are mobile or anchor mobile features such as dislocations. While the details of the grain boundary hardly matters, we conclude that the overall textural features and not the local properties of solid grain boundaries dominate the elastic or an-elastic response.

In this paper we exclude features such as melts on interfaces and refer to Hiraga et al. (2002) for intergranular melt phases with a characteristic thickness in the range of 0.5–10 nm and de Kloe et al. (2000), Tan et al. (2001) and Faul and Jackson (2004) for careful analysis of melt-bearing systems involving olivine. While it is possible to extract information about the melt, we focus here on melt-free interfaces without grain boundary sliding or any other movement which trivially leads to dissipation of strain energy. Instead we wish to discuss structural features of static, dry interfaces and ask the question whether they

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could contribute to the an-elastic behaviour of mineral assemblies.

Some examples may illustrate the relevant textural features. Mono-crystalline quartzite, agate and sandstones form composites with mainly one constituent, namely quartz. Texture equilibrated, coarse-grained material with chemically clean grain boundaries, can be confidently expected to display isotropic elastic constants as predicted from effective medium theories such as the Hashin-Shtrikman averaging formula (which, in quartzite, is not far away from the more crude Hill, Voigt and Reuss schemes). Without structural relaxations textural equilibrium exists only for one temperature, however. At all other temperatures the highly anisotropic thermal expansion of the quartz grains can generate excessive stresses in the sample which, sometimes, leads to the spontaneous destruction of a sample under heating. While these effects are mild at temperatures far away from the transition point between α and β quartz at 851 K, they become more pronounced when a sample is heated towards and beyond this temperature. Inter-granular stresses could be calculated in a reasonable approximation by Pertsev and Salje (2000) predicting that for small enough grains the nature of the transition is changed from a stepwise transition to an almost continuous one. These ideas agree with experimental observations by Rios et al. (2001) while another, even more extreme outcome of such stress fields might be that the interfaces between grains are amorphised (Page et al 2004) or structurally modified so that novel SiO_2 interfacial features may be generated. If we now extend this idea to allow the minerals to include voids and mobile species such as hydrogen, it becomes clear that the elastic properties of materials even as simple as agate are far from being defined as a 'material property' but reflect local stress fields, thermal history and grain sizes which may modify the bulk and shear moduli of single crystals significantly and even limit the usefulness of experimental studies unless such dependencies are much better understood than is presently the case. In this sense, minerals can behave similar to shape memory alloys where the thermal history is of predominant importance (Salje et al. 2007; Khalil-Allafi et al. 2005). Such effects are unlikely to occur at sufficiently high temperatures and sufficiently low heating/cooling rates where textural equilibrium can be maintained over a larger temperature interval.

The second example relates to the interface between crystalline zircon and locally amorphised regions. Such regions became glassy through radiation damage in metamict sample. While the hydrous species in such materials partition (Salje and Zhang 2006), the overall chemical composition of the samples remains uniform. The elastic moduli soften by about 50% in amorphised material as compared with the crystalline starting material. Simultaneously the specific volume of metamict zircon increases by almost 20%. While the actual swelling process is complex with percolation of interfaces (Trachenko et al. 2000, 2003; Zhang et al. 2000; Rios et al. 2000; Salje et al. 1999), one can estimate the effect of interfaces towards the elastic softening by a simple scaling argument (Salje 2007). In terms of a simple mixing model the volume scales as

$$V = x\ V_{\text{amorphous}} + (1-x)\ V_{\text{crystalline}} + \ x(1-x)\Delta V \qquad (1)$$

where x is the amount of amorphous material and ΔV is the excess volume related to boundaries between crystalline and amorphous parts of the sample. If the excess volume extends over the full sample we may put

$$\Delta V = V_{\text{crystalline}} - V_{\text{amorphous}} \qquad (2)$$

so that the total volume scales quadratically in x rather than linearly:

$$V = V_{\text{crystalline}} + x^2(V_{\text{amorphous}} - V_{\text{crystalline}}) \qquad (3)$$

while generally we expect a grain size dependent scaling parameter S between the linear and quadratic component

$$V = V_{\text{crystalline}} + [(1-S)x + Sx^2](V_{\text{amorphous}} - V_{\text{crystalline}}). \qquad (4)$$

Since the idea of grain boundary sliding was introduced (Bowden and Taylor 1950; Israelachvili 1992) it is assumed that the scaling of S relates to the interfacial contribution d^{-m} where m is the scaling exponent of the grain size d (*see also* Faul and Jackson 2005; Frost and Ashby 1982). For thin interfaces the surface scaling is a two-dimensional subspace with $m = 2$ but this cannot hold for either small grains or materials close to structural instabilities where the surface relaxations extend deeply into the grain (Houchmanzadeh et al. 1992; Conti and Salje 2001; Novak and Salje 1998a, b). A similar argument was put forward by Frost and Ashby (1982) where scaling in the case of rheological amplitudes and timescales, the enhanced interfacial diffusion, can lead to mixtures of grain size scaling with $d^{-2}\ (1 + a/d)$ where the parameter a depends on the interfacial thickness and a ratio of shear constants in the bulk and in the grain boundary. Note that in a second order phase transition the thickness of the surface layer diverges at the transition point as the correlation length so that interfacial layers as the thickness of twin boundaries (Chrosch and Salje 1999; Wruck et al. 1994) invade the entire grain. In this case m reduces to zero because no bulk contribution exists. A grain size exponent for creep is predicted to be 3 for diffusional creep when the diffusion happens along the grain boundaries. Similar arguments can be made for the volume scaling and the corresponding scaling of the effective elastic moduli as seen below. Surface exponents are, thus, not trivially 2 but can range between 0 and 3 (Faul and Jackson 2005, 2007)

The third example relates to the difference in elastic behaviour between laboratory experiments and field observations when several mineral phases are involved. While such differences are already expected in our first example, a recent study of the phase mixtures between forsterite and enstatite in the laboratory experiment by Ji and Wang (1999) showed bulk moduli which were incompatible with seismic observations. The question then arose that if laboratory samples, even under the most careful preparative conditions, possess the same interfacial strength as equilibrated samples in the appropriate geological environment. In the case of the forsterite–enstatite interface an analysis of the experimental data showed indeed that soft interfaces could explain the observed inconsistencies (Salje 2007).

Before we discuss such possible mechanisms we need to exclude one class of extreme an-elastic behaviour which defines ferroelasticity (Salje 1993). In this case, internal interfaces such as twin boundaries move with little restoring forces through samples when external stresses are applied (Lee et al. 2006). The effective elastic bulk and shear moduli are then completely dominated by such moving interfaces and reductions, in stiffness by one order of magnitude, are common (Kityk et al. 2000; Harrison et al. 2004). The elastic moduli cease to be materials parameters and largely depend on the mobility of interfaces, boundary conditions and the internal structures of interfaces. Such effects have been widely researched and will not be described any further in this paper. If such effects play a role in the geophysical context, say for the perovskite and post-perovskite phases in the Earth's mantle, we have virtually no predictive power for the quantitative values of their effective elastic moduli nor the Q-values for wave propagation unless quantities such as the pinning coefficients, the wall energies and entanglements of interfaces are known much better than is presently the case. The more likely movement of grain boundaries under weak stress fields, possibly assisted by the transport of hydrogen, will also be excluded from this paper. Here we focus on the discussion of the hypothesis whether soft elastic, dry, static surface layers can influence seismic wave propagation significantly.

The issue of interfacial contributions to elastic behaviour has been discussed for several decades (Green and Zerna 1954) and two new recent developments show promising progress. Firstly, large-scale computer simulations have led to a much better understanding of simple microstructures, self-organisation and structural relaxations. Such understanding correlates with analytical work, as summarised extensively by Milton (2002), so that we now know that 'standard models' the coated sphere model (Fig. 1), various percolation models, the brick wall model (Fig. 2), visco-elastic interface models, etc. allow us to predict certain trends in experimental observations. In the geological literature, Watt (1988) already used the Hashin-Shtrikman bounds to good effect for dense isotropic polycrystals. Here we will use the same model to include a variety of interfaces.

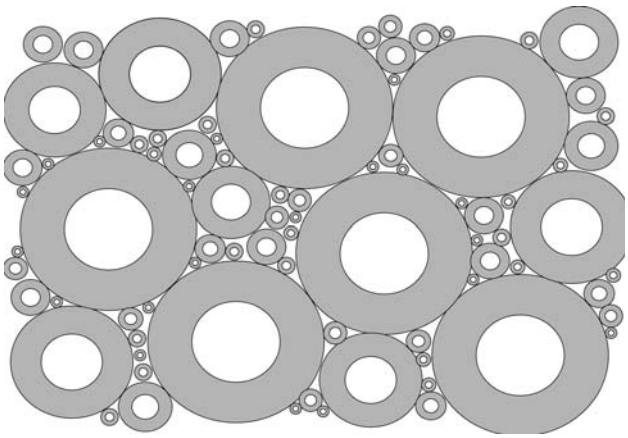

Fig. 1 The coated sphere model (space is filled in a series of *spheres of diminishing diameter*, each sphere is coated with a *rim*, no interpenetrating is allowed in three dimensions)

The second encouragement is related to the fact that seismological observations can act as a guide to the interpretation of solid state processes under extreme conditions (Faul and Jackson 2005; Jackson et al. 2006). The non-trivial question is, as often in elasticity, to what extent strain–stress relations remain linear under these conditions. While it is clear that linearity is not obeyed for large stresses for virtually all materials, non-linearities for small stresses exist also for large classes of materials, such as elastomers (Adams and Warner 2005) or ferroic materials (Salje 1992). Once stresses are so small that relevant atomic displacements are smaller than thermal vibrational amplitudes, nonlinearities due to surface relaxations dominate, although

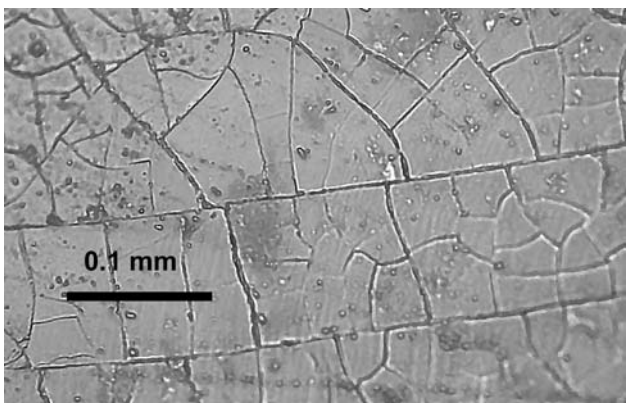

Fig. 2 Shear moduli can be significantly weakened in brick-wall type texture pattern where percolating planes allow easy sliding of layers against each other. Here a brick-wall pattern is shown for metamorphically altered metamict zircon

it is very hard to measure such effects experimentally. Non-linearities are enhanced if defects contribute to random fields in the surface. Typical examples are Random Field Ising models (Roters et al. 2005) with a large variety of creep and de-pinning regimes (Salje et al. 1983). It may even be asked what the physical meaning of interfacial melting is if its effect is to ease shear between two interfaces by less than one atomic diameter for a grain size of 1 mm. Experimental evidence for the existence of 'exotic' interfacial layers is rare, however. Page et al (2004) have analysed their neutron diffraction signals from a Fontainebleau sandstone in terms of models which contain a glassy interface between quartz grains. They claim to have observed 5–10% of a glass phase with grain sizes of 0.1–0.25 mm in diameter. The glass rim of the grains is then well in the macroscopic range and unlikely to be the result of grain–grain interactions in particular as the porosity of their sample was 24% (Darling et al. 2004) while no additional TEM based-evidence was found for such a claim. Nevertheless, the existence of such massive interfaces may give encouragement to the idea that thinner, structurally determined interfaces exist and modify the macroscopic elastic response of mineral assemblies in the context of seismic wave propagation. Linearity, on the other hand, was found in calcite rocks at seismic frequencies by Jackson and Paterson (1987) for strains down to 3×10^{-8}. It is of great interest to see whether non-linear responses can be observed in other materials, perhaps at lower temperatures.

It is the purpose of this paper to explore which fundamental processes are likely to lead to elastic softening and an-elastic behaviour under the conditions that interfaces do not move (such as in ferroelastic materials or mobile grain boundaries including grain boundary sliding) but contribute only via their own elastic softening. The term 'elastic' will be used in the next section to indicate the linear part of the strain–stress curve ignoring possible non-linearities for extremely small strain variables. It will be shown that macroscopic softening is mostly restricted to sub-micron grain sizes but that visco-elastic and 'rubber-like' interfaces can provoke pronounced softening for larger grain sizes. While it will be argued in this paper that typical grain sizes where interfacial effects play a major role are in the sub-micron range it needs to be born in mind that much larger grain sizes matter when the materials undergo structural phase transitions. A typical example is the martensitic phase transition in Ti-Ni alloys where Saburi et al. (1984) showed that pseudo-elastic behaviour (i.e. closed strain–stress loops) can only be observed in polycrystalline materials but not in single crystals where the stress free condition will always reflect the full spontaneous deformation of the sample. Reduction in grain size is very effective in improving pseudo-elasticity with linear strain-stress curves for small stresses for grain sizes less than 50 microns and rather small macroscopic spontaneous strains already for grain sizes below 1 mm. Nucleation effects can be dominant for even bigger grains (e.g. Cu–Al–Ni) of the order of 1 cm so that the term 'small grain sizes' has to be understood in this paper relative to the physical processes rather than in absolute terms. While these mechanisms may matter, they are still not sufficiently well understood to be extrapolated to extremely small driving forces as applicable for seismic wave propagation. The second common assumption, namely the use of grain size exponents to extrapolate from small grains in laboratory experiments to larger crystals in nature, is also argued to be highly speculative and not in accordance with the known grain size dependences of some standard models.

Soft interfaces and isotropic spherical grains

The elastic behaviour of assemblies of elastically isotropic minerals can be calculated from simple effective medium theories. The same is true to some approximation for anisotropic minerals which will form a statistically averaged isotropic matrix. We now ask how such assemblies can lead to soft interfaces. In order to maintain the focus on the physics of the interfaces, we assume that anisotropic thermal expansion and compressibility of the grain is irrelevant whereby this condition can be fulfilled either by atomistically isotropic materials or grains which are themselves already statistically averaged.

The most popular model for the description of such assemblies is the coated sphere model which was described in detail by Hashin (1962). It is one of a small number of models where the effective bulk modulus can be calculated exactly. Grabovsky and Kohn (1995a, b) extended the model to coated ellipsoids while the most general geometries can be treated within the Hashin–Shtrikman bounds (HS). For small elastic displacements we use HS and allow both the grains and the interfaces to relax elastically. The elastic bulk and shear moduli lie between the bounds:

$$\begin{aligned} &f(r)\kappa_1 + (1-f(r))\kappa_2 - f(r)(1-f(r))(\kappa_1-\kappa_2)^2/ \\ &[(1-f(r))\kappa_1 + f(r)\kappa_2 + 4\mu_1/3] > \kappa* > \\ &f(r)\kappa_1 + (1-f(r))\kappa_2 - f(r)(1-f(r))(\kappa_1-\kappa_2)^2/ \\ &[(1-f(r))\kappa_1 + f(r)\kappa_2 + 4\mu_2/3] \end{aligned} \tag{5}$$

and

$$\begin{aligned} &\mathrm{f(r)}\mu_1 + (1-f(r))\mu_2 - f(r)(1-f(r))(\mu_1-\mu_2)^2/ \\ &[(1-f(r))\mu_1 + f(r)\mu_2 + \{(9\kappa_1+8\mu_1)\mu_1/(6\kappa_1+12\mu_1\}] \\ &> \mu* > f(r)\mu_1 + (1-f(r))\mu_2 - f(r)(1-f(r))(\mu_1-\mu_2)^2/ \\ &[(1-f(r))\mu_1 + f(r)\mu_2 + \{(9\kappa_2+8\mu_2)\mu_2/(6\kappa_2+12\mu_2\}] \end{aligned} \tag{6}$$

for spherical particles. The bulk and shear moduli for the phases 1 and 2 are κ_1, κ_2, μ_1, and μ_2, respectively. Here we treat the phase 2 as the interface and $f(r)$ as the volume proportion where r is the radius of a spherical grain. With typical values for silicate phases of $\kappa_1 = 200$ GPa and $\mu_1 = 100$ GPa and assumed interfacial values in the order of $\kappa_2 = 20$ GPa and $\mu_2 = 10$ GPa the calculated values in Figs. 3 and 4 show that effective softening starts at ca. 0.1% of the bulk being occupied by interfaces. Experimental values of interfaces range around 10 nm so that one expects softening to become relevant for grain sizes below some μm. No simple power law dependence exists in this limit although linerity would fit the three point correlation moduli over a very limited range of grain sizes (Fig. 4). We have used here the three-point bounds to improve the HS bounds using 3 point correlations (Milton 2002).

Thin interfaces

So far soft interfaces only matter for relatively small grain sizes because the effect scales with the volume fraction of the interfaces. While this scaling remains correct in the case of imperfect and visco-elastic interfaces we find in the limit $G_{\text{interface}} \to 0$ that the effective modulus becomes small even for small volume fractions of the interfacial layer. In the extreme case of $\mu_{\text{interface}} = 0$ the inclusions are decoupled from the matrix and act as voids when fully relaxed (i.e. in the limit of long times). Reasonable physical models of imperfect interfaces as a first step towards freely sliding interfaces have been considered by Mal and Bose (1975), Benveniste (1987) Chatterjee and Kibler (1979), Achenbach and Zhu (1990) and, more recently, by Hashin (1992).

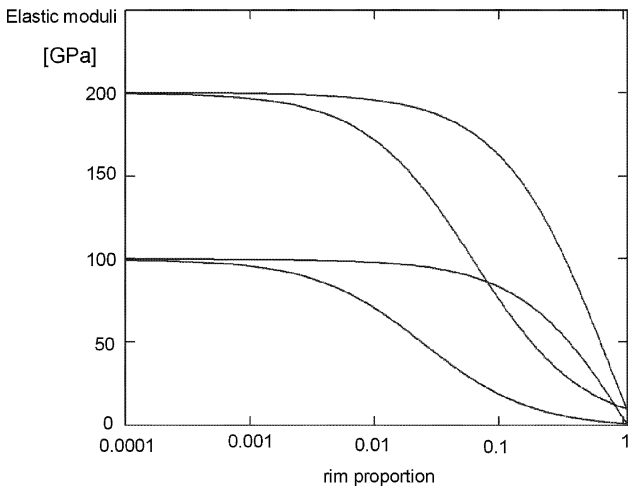

Fig. 3 Elastic softening of the bulk and shear moduli in the coated sphere model as a function of the volume proportion of the grain boundary relative to the grain

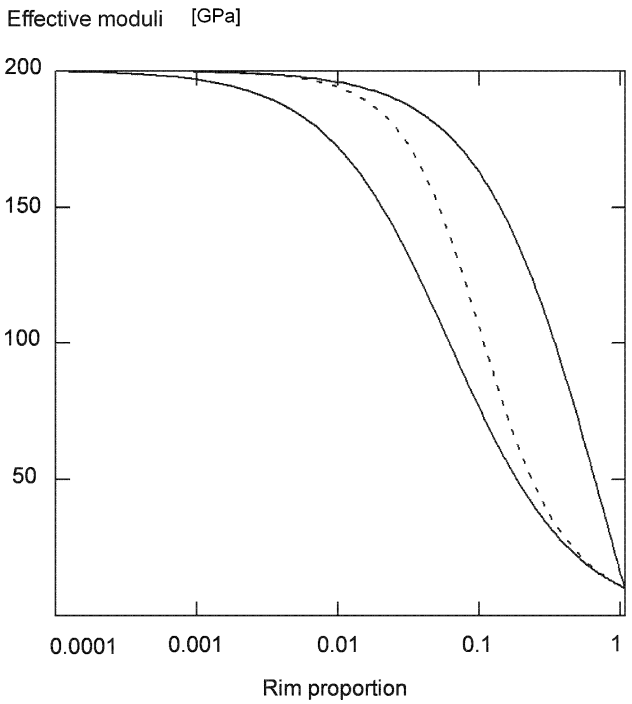

Fig. 4 Effective compressibility as upper and lower Hashin Shtrikman bounds (see Fig.3) and as 3-point correlation (*dotted line*) for a realistic case of a silicate mineral

While in the 'perfect' interface condition the displacement and traction fields are continuous across the boundary, this condition is dropped in case of imperfect boundaries. It is assumed instead that normal and tangential interface displacements jump with amplitudes proportional to their associated traction components. This requires that thin interfaces are described by interface parameters D which describe the replacement of the chemical bonds by 'springs' with different spring constants in tangential and normal directions (D_n, D_s and D_t are the principle tensor components of spring constants with directions normal n, and tangential, s and t, to the interface). For spherical isotropic grains of phase 1 and phase 2 with the rim attached to phase 2 Hashin (1992) has shown that these parameters translate for the upper bounds of κ and μ to α_κ and α_μ between zero (perfect interface) and infinity (unbounded interface) as

$$\begin{aligned} \kappa^+ &= \kappa_1 v_1 + \kappa_2 v_2/(1 + a_\kappa), \\ \mu^+ &= \mu_1 v_1 + \mu_2 v_2/(1 + a_\mu). \end{aligned} \tag{7}$$

This means that the upper limit for highly bonded interfaces is equivalent to the results above while unbonded grain boundaries act as voids of the grain (upper bound of an assembly with voids). The lower bounds are more interesting for the current discussion. They can be formulated explicitly in terms of the inverse length scale (or interface 'density') $\xi =$ interfacial surface/ total

volume. With the indices n and s, t indicate the normal and two tangential interfacial parameters one finds

$$\kappa^{-} = v_1/\kappa_1 + v_2/\kappa_2 + \xi/D_n)^{-1} \quad (8)$$

and

$$\mu^{-} = (v_1/\mu_1 + v_2/\mu_2 + 2/5\xi\{2/3D_{\rm n} + 1/D_{\rm s} + 1/D_{\rm t}\})^{-1} \quad (9)$$

Perfect interfaces will again reduce to the lower bounds of the two phase mixture while imperfect interfaces with shear instabilities correspond to the limit of large D_n while D_t and D_s are small. This shows that the bulk modulus changes little while the shear modulus softens. The grain size dependence enters via ξ which becomes $4\pi\Sigma d^2/V$ for spheres where the sum extends over all spheres and V is the volume. The total scaling is then $3v_2/d$ where v_2 is the filling factor of phase 2 when the interface is a constituent related to phase 2. If the interface exists only between different phases the scaling changes to the probability of connection between two phases which is v_1v_2 or, ignoring the volume contribution of the interface, $v_1(1-v_1)$ as in Eq. 1. If D is then related to the difference of the moduli between the two phases one recovers scaling as in Eq. 4. The Voigt average would then also contain an interfacial term equivalent to the S-dependence in Eq. 4.

Hashin (1992) considered very soft interfaces with $\mu/dD_{\rm s} = 10$ attached to phase 2 which would lead to reductions of μ in mono-mineral composites by almost one order of magnitude. In materials such as olivine one may expect that the length scale set by the ratio $\mu_i/D_{\rm s} = t_{\rm i}$ where $\mu_{\rm i}$ is the effective shear constant of the interface and $t_{\rm i}$ is the thickness of the interface. The Poisson's ratio of the interface is assumed to be 0.375 as in the model of Hashin with $D_n = 5D_s = 5D_t$. We can now estimate the grain size dependence with $t_{\rm i} = 1$ nm, a filling factor of 20%, $\kappa_1 = 200$ GPa, $\kappa_2 = 150$ GPa, $\kappa_{\rm i} = 1$ GPa, $\mu_1 = 100$ GPa, $\mu_2 = 80$ GPa and $\mu_{\rm i} = 0.5$ GPa. The resulting dependence on the grain size is shown in Fig. 5 where all lengths are measured in units of $t_{\rm i} = 1$ nm. With this assumption and rather typical elastic moduli one obtains significant grain size dependence in the sub-micron regime while larger values of $t_{\rm i}$ may shift this length scale to larger grain sizes. This shift appears to be limited by realistic thicknesses of interfacial layers (say, below 10 nm) to perhaps one order of magnitude so that significant softening is still unlikely for grain sizes of some mm. No simple grain size exponent exists for imperfect interfaces in Fig. 5 which would allow a meaningful extrapolation from experimental values of small grain sizes towards much larger values unless the bulk contributions are removed and the interface dependent part is evaluated individually.

Hashin (2002) has discussed numerical solutions for coated fibres. He reported significant softening for ratios of $\mu_{\rm i}/\mu_1$ of 0.01 to 0.001 and rim to grain diameter ratios of 0.001 or smaller. With rim thicknesses of (10 nm the relevant grain diameters would be below 10 μm while stiffer interfaces would eliminate the softening very rapidly. The largest effect was found in the transverse shear stiffness which reduced strongly for interfacial shear constants of 10% of the bulk values and grain diameters of ca 500 nm rim thicknesses. No universal power law dependence for the extrapolation of the grain size dependence was found.

Finally we give a simple estimate for the effective bulk modulus within the previous changes bounds as

$$\kappa* = \kappa_1 + f/[1/(\kappa_e - \kappa_1) + 3(1-f)/(3\kappa_1 + 4\mu_1)] \quad (10)$$

where the interfacial bulk modulus $\kappa_{\rm e}$ is

$$\kappa_e = \kappa_2/(1 + 3\kappa_2/aD_{\rm n}) \quad D_{\rm n} = (\kappa_{\rm i} + 4\mu_{\rm i}/3)/\delta \quad (11)$$

The index 1 is the matrix and 2 is the inclusion, i refers to the interface attached to phase 2.

Hashin (1991) argued that the viscoelastic counterpart of the jump conditions at the interface can be written simply as

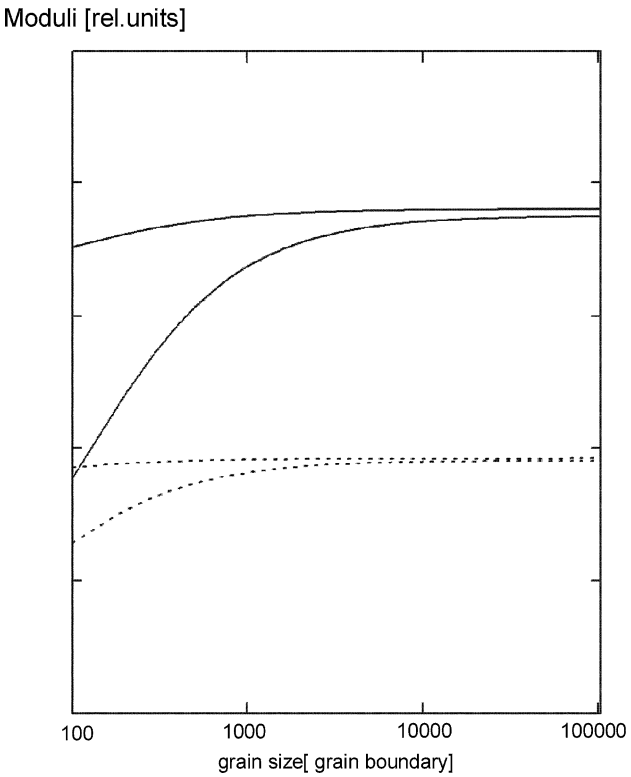

Fig. 5 Grain size dependence of the bulk modulus (*upper* and *lower bounds*, *solid lines*) and shear modulus (*upper* and *lower bounds*, *dotted lines*) for parameters given in the text. The length scale is given in units of the interfacial thickness which can be estimated to be 1 nm. Interfacial softening occurs in this case for grain sizes smaller than some 5 μm

a time derivative of the jump convoluted with the time-dependent interface function $D(t\text{-}t')$. The effective elastic moduli are then calculated in exactly the same way as the time-independent functions where each value is replaced by its Laplace transform multiplied by the frequency. This quantity was called TD (transform domain) by Hashin (1965). This means that the interfacial effects in the initial state ($t = 0$) and the final state ($t =$ infinity) are the effective medium averages when the equivalent values of $D(0)$ and $D(\text{inf})$ are used. The most simple time dependence of the stress–strain relation is described by the Maxwell model

$$\delta e_{\mathrm{kl}}/\delta t = s_{\mathrm{kl}}/2\eta^{\mathrm{i}} + [\delta s_{\mathrm{kl}}/\delta t]/2\mu_{\mathrm{I}} \tag{12}$$

where the index i refers again to the interface. This relation can be written in the TD domain as

$$s_{\mathrm{kl}} = 2\eta\omega/[1 + \tau_{\mathrm{i}}\omega]e_{\mathrm{kl}} \tag{13}$$

where italic letters denote quantities after Laplace transform and $\tau_{\mathrm{i}} = \eta_{\mathrm{i}}/\mu_{\mathrm{i}}$ is the time constant for the flow. This time constant is defined by the ratio between the viscosity and the (very small) shear modulus of the viscous interface. Such time constants can be very long even under conditions as typical for laboratory experiments and can easily be mistaken as local relaxations as typically seen in Snoek-relaxations. The time constant and, thus, the creep strength depends in this approach sensitively on the ratio $\eta_{\mathrm{i}}/\mu_{\mathrm{i}}$ which in turn depends sensitively on the defect concentration and the confining pressure of a grain boundary. It is expected, therefore, that even small amounts of melt or hydrous species will facilitate creep. This brings the behaviour close to diffusion assisted grain boundary sliding and, for sufficiently long timescales, to steady state diffusional creep. Experimentally, such behaviour was observed in olivine by Faul and Jackson (2007) (see also Yoshino et al. 2007; Schmeling 1985).

The interfacial shear modulus in the transform domain can now replace the static interfacial modulus so that the structure of the solutions shows the typical viscous decay of the shear modulus from the initial, elastic limit to the final limit which can equally be understood as an elastic limit where all inclusions are replaced by voids. This shows that in the Maxwell model the long time limit is that of a porous medium with the same geometry as in the initial material. Examples for fibres and sphere assemblies where discussed by Hashin (1991).

The fingerprint of the Maxwell model of viscous interfaces is that the bulk modulus shows little time dependence while the shear modulus is expected to be more strongly time dependent. The time constant depends on temperature and pressure. The initial, short time behaviour is approximately exponential so that the frequency dependence of experimentally observed strain relaxation is expected to be not too far from the Debye type.

The Maxwell model, as all continuums models, could have limited value in the case of small displacements where atomic modelling is expected to be essential. In case of related continuums models, such as Landau theory of interfaces and their lateral movement in ferroelastics (Lee et al. 2003; Calleja et al. 2003) the surprising answer is that even for very small distances (say of atomistically thin interfaces) the predictions of Landau-type theories still hold well. A similar observation was made in nano-tribology where the predictions of the Johnson, Kendall, Roberts (JKR) theory and the initial Hertz theory are surprisingly valid when measured on a sub-nanometer scale (Carpick et al. 1996; Hertz 1881; Johnson 1987; Johnson et al. 1971).

While the validity of continuum models is greater than one might expect it is not necessarily true that these findings can be extrapolated to real geological situations. The external load under geological conditions may be too large to allow friction movement to occur. Experimentally, lateral displacements of ca. 0.1 nm have been observed for shear forces of some nN (Carpick et al. 1996). In areas of underlying shear motion and areas where fluid-like interfaces exist (because of melting or the existence of water or other hydrous species) detailed model calculations even predict a regime of multiple slip motion of surface atoms during frictional flow (Medyanik et al. 2006).

The assumption that viscous interfacial layers of atomic thickness and friction-related processes on the same length scale exist and are visible in seismic experiments may also be argued in view of other origins of low-viscosity interfaces. The first idea was probably that of Aubry (1983) who conjectured that laterally stiff surfaces with incommensurate atomic arrangements should have vanishing friction. Grains of millimetre size and in textural equilibrium with fully relaxed surfaces may, indeed, show such features locally. Temperature and pressure effects can also reduce friction dramatically when the inter-grain movements fall below a critical velocity. The critical velocity itself increases strongly with temperature because interfacial jumps are thermally activated for low velocities and, thus, reduce the effective viscosity of the interface. This may hold under conditions of seismic wave propagation. A simple thermal activated process with a thermal activation energy in the range of defect energies is then observed macroscopically. This situation is similar to defect migration in the bulk (Krylov et al. 2005). Interfacial thermal activations of surface waves or external sound waves have also been shown to massively reduce friction and hence reduce viscosity with relevant forces in the pico-Newton regime. While these phenomena are likely to occur only under resonance conditions (low frequency excitations of the interface), it was argued that such excitations occur naturally in regions of tectonic instabilities (Socoliuc et al. 2006).

Finally, the relaxational non-linear elastic response of zircon at high temperatures and pressures was understood in terms of local relaxations, probably related to the interfaces between amorphised grains regions and a crystalline matrix (Trachenko et al. 2007). The current treatment maintains many ideas of this previous theoretical approach while our prediction of the time dependence (via the double LT) is more general and may not apply when many local centres relax in a correlated fashion. Trachenko (2007) argued that time dependences can then be logarithmically slow while even this result would not significantly change the consequences for seismic observations of such correlated processes.

Extrapolations of grain sizes and amplitudes from laboratory experiments

One of the banes of the application of laboratory experiments to geophysical situations is not only the difficulty of working at high temperatures and pressures but also the extrapolation of two relevant length scales. One length scale is the grain size and its relation to the effective grain boundary. As argued above, temperature effects can increase the thickness of 'grain boundaries' even when the grain size remains constant. Pressure will change other parameters such as t_i dramatically, again without any change of d. Simple grain size scaling exponents have been traditionally used to capture dependences in creep experiments with well-defined diffusional pathways (e.g. $m = 3$ for grain boundary diffusion) while dimensional estimates would lead to approximations of $m \ll 3$ as shown in examples above. In all explicit solutions given in this paper, no simple power law was found so that the numerical fit of experimental data over large ranges of grain sizes appears to be highly problematic. In general, the grain size dependence becomes weaker for elastic effects (but not necessarily for visco-elastic softening) for grain sizes above some 50 μm. Grain size scaling becomes even more problematic when volume effects (e.g. dislocation movements for dislocations near the grain boundaries) or grain size invariant processes (movement of internal surfaces, twin boundaries. etc.) are involved. It may be concluded that extrapolations from the micrometer length scale to the milli meter length scale are very uncertain.

A final example for non-linear strain stress curves which may play a role under geophysical conditions occurs when the interfacial materials contains structural cross linking similar to rubber or certain glasses which can not be captured in classic linear analysis. To illustrate this point let us consider the usual composite sphere arrangement (Hashin 1985). Let a body deform with a displacement $u_i(X)$ as

$$u_i(X) = (\lambda - 1)X_i$$

where large letters denote initial coordinates and small letters denote current coordinates (so that $x_i = \lambda X_i$). In an elastic and isotropic body there exists a strain energy function W of the strain invariants I1, I2, and I3 associated with the Langevin strain tensor (Green and Zerna 1954). These authors have shown that the strain tensor $\sigma_{ij} = \sigma\ \delta_{ij}$ is given by the derivatives

$$\sigma = 2(\delta W/\lambda\delta I_1 + 2\lambda\delta W/\delta I_2 + \lambda^3\delta W/\delta I_3).$$

where the invariant functions for isotropic media become functions of(λ alone:

$$I_1 = 3\lambda^2\ I_2 = 3\lambda^4 \text{ and } I_3 = \lambda^6.$$

We now consider a material with bulk modulus κ_1 which is surrounded by a rubber-type matrix which obeys the Mooney-Rivlin energy density

$$W = C_1(I_1 - 3) + C_2(I_2 - 3).$$

While the interfaces are non-linear the inclusions remain elastically hard and linear so that the effective bulk modulus remains for an incompressible elastic the same as the bulk modulus of the mineral alone, ignoring the interface with

$$\kappa* = \kappa_1/c$$

where c is the filling factor. The shear modulus, in particular, depends on $C1$ and $C2$ which leads to non-linear strain stress curves (Hashin 1985). For large values of $C1$ and $C2$ this dependence would lead to a significant asymmetry in the strain stress relationship with stiffening for compression and softening for elongation of the inter-grain layer. As Hashin (1985) already pointed out, this effect can lead to a drop in moduli with extreme asymmetry when the interfacial layer decouples for large strains from the grain (say in a slip movement). In extreme cases the interfaces could fail to bond the grains even though the interfaces themselves remain nearly incompressible. This would lead to nearly incompressible fluids with extreme asymmetries between the compression and expansion branches of the strain–stress curves. While such instabilities are unlikely to occur under high confining pressure, the inherent nonlinearity may still matter for wave propagation.

Conclusion

Low-frequency wave propagation with low amplitudes may well strike physical features which are not encountered under the usual laboratory conditions. Explicit mechanical models for grain boundary softening and hardening do not lead to simple extrapolation equations,

such as simple power laws, over large intervals of grain sizes. While such predictions can be verified with currently available experimental tools it is much harder to investigate the dependence of elastic response functions at low frequencies, high T, and high P as a function of the wave amplitude. It may be possible to construct experimental conditions where the wave absorption is measured as a function of frequency over a sufficiently wide frequency band and where the elastic moduli are simply calculated via the Kramers–Kronig relationship. Non-linear response is then expected to generate deviations from the Kramers–Kronig relationship which can be observed if the real and imaginary parts of the moduli are measured independently over a very large frequency range. The first work by Jackson et al (2000) confirmed that 'essentially linear' behaviour exists for viscoelastic relaxations in iron. Further work in other systems and for wider frequency ranges would be desirable.

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